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Electronic Supplementary Information (ESI)

Nanoporous Black Silicon Photocathode for H_2 Production by Photoelectrochemical Water Splitting

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Experimental Detail

1. Fabrication of Nanoporous Si photoelectrodes:

300 μm thick p-type (100) float-zone Si wafers with 2.5 Ω·cm are tested as photocathodes. After RCA cleaning, an ohmic contact is formed at the back of the wafer by applying commercial Al paste (Ferro® FX 053-038) and firing at 800°C. During this high temperature Si-Al alloy formation, a heavily-Al doped layer, about 5- to 10-μm thick, forms between the Al paste and the p-type Si. This p^+ layer serves as a back surface field that improves the minority carrier lifetime. The polished Si photoelectrode is complete at this step, but processing continues for the nanoporous photoelectrode. We apply paraffin to the backside ohmic contact to protect it from metal-assisted etching solutions. The nanoporous Si is formed at the exposed front surface by immersing it in 0.4 mM $HAuCl_4$ and then adding an equal volume of 1:5:2 HF: H_2O_2:H_2O solution and reacting for 3 minutes before a de-ionized water rinse. The remaining Au nanoparticles at the bottom of pores after etch are then removed by an I_2/KI solution (25 g/L of I_2 and 100 g/L of KI in H_2O). Finally, the paraffin film is removed with trichloroethylene and the photoelectrode is rinsed with ethanol and isopropanol. We measure the total reflectance spectra of the nanoporous Si samples

with the Al back contact in air, using a Varian Cary 6000i spectrometer with an integrating sphere.

2. Photoelectrochemical characterization:

For PEC measurement, the backside Al layer of the Si is contacted with silver paint and connected to Cu wires encapsulated in a glass tube. The exposed backside, edges, and some part of the front of the electrodes were sealed with an industrial epoxy (Loctite 9462); only a well-defined area of the front Si surface was exposed to the electrolyte [1]. Prior to the PEC measurement, any native oxide on the Si photoelectrodes is removed by a 60 s dip in a 10% HF solution. A custom-built Pyrex glass vessel with flat windows was used as the PEC cell. A tungsten-halogen lamp (250 W, Oriel) with an IR cutoff filter is the light source; its intensity closely simulates 1-sun AM1.5 illumination, as calibrated with a Si photodiode (Solarex, Serial No. 147). 0.5 M sulfuric acid (ACS reagent grade, J.T. Baker) is the electrolyte. Unless otherwise noted, a small amount (2 g/L) of Zonyl FSN-100 (DuPont) is added as a surfactant to promote H_2 bubble evolution. Ag/AgCl (3M KCl) and Pt foil are used as the reference electrode and counter electrode, respectively. Electrochemical measurements use a potentiostat (Solartron 1287) interfaced with a computer running CorrWare® for instrument control and data collection. Before each measurement (e.g., Figs. 2 and 3), the photocathodes are treated by application of -1.5 V vs. Ag/AgCl (3M KCl) for 5 minutes under illumination to stabilize the surface. The photoelectrochemical *j-V* curves are ramped from – 1.5 V vs. Ag/AgCl (3M KCl) to + 0.05 V vs. OCP (open-circuit potential) at a rate of 20 mV-s^{-1}. We measure IPCE with illumination from a W lamp (100W) filtered through a monochromator (Photon Technologies International) from 400 nm to 750 nm, at a potential of -1.0 V vs. Ag/AgCl (3M KCl). A Si photodiode (Hammamatsu) with known quantum efficiency is used to calculate the IPCE of the nanoporous and polished Si photocathodes.

References

1. A. Bansal and J. A. Turner, *Journal of Physical Chemistry B*, 2000, **104**, 6591-6598.